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(54) **Processes of bleaching fabrics**

(57) The present invention relates to processes of bleaching fabrics wherein fabrics are contacted with a liquid bleaching composition comprising a hypohalite bleach, from 0.1% to 20% by weight of the total composition of a surfactant and from 0.001% to 10% by weight of a stabilising agent selected from the group consisting of radical scavenger, chelating agent and mixture thereof, in its diluted or neat form. Advantageously, effective stain removal performance is delivered upon ageing of the composition when used in any laundry application.

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DescriptionField of the invention

- 5 **[0001]** The present invention relates to the bleaching of fabrics, including hand and machine laundry methods, with liquid hypohalite bleach-containing compositions.

Background of the invention

- 10 **[0002]** Bleaching compositions are well-known in the art. Amongst the different bleaching compositions available, those relying on bleaching by hypohalite bleaches such as hypochlorite are often preferred, mainly for performance reasons, especially at lower temperature.

- [0003]** However, there are some limitations to the convenience of hypohalite bleach-containing compositions, especially when it is desired to have good stain removal performance on the fabrics treated therewith on top of the fabric whiteness performance. This is even more a problem when aged compositions are used, i.e. when the compositions are used in a laundry application after prolonged periods of storage after their manufacturing.

- [0004]** It has now been observed that when it is desired to incorporate surfactants in a liquid hypohalite bleach-based composition, the resulting composition generally shows a poor chemical stability upon ageing of the composition, resulting in low stain removal performance of the composition when used in any laundry application after prolonged periods of storage. Indeed, upon prolonged storage periods the surfactants may be decomposed by the hypohalite bleach present in such a liquid hypohalite bleach-based composition, and thus may lose their stain removal potential. This surfactant decomposition can be accelerated by product exposure at high temperature or by raw material impurities.

- [0005]** It is therefore an object of the invention to address the issue of poor stain removal performance on fabrics when bleached with aged hypohalite bleach-containing compositions.

- [0006]** The Applicant has thus now surprisingly found that this issue is efficiently addressed when the liquid bleaching composition used to bleach fabrics comprises a hypohalite bleach, a surfactant and a stabilising agent selected from the group consisting of a radical scavenger, a chelating agent and a mixture thereof. Indeed, it has been found that the presence of such a stabilising agent in a liquid bleaching composition comprising a hypohalite bleach and a surfactant, provides improved stain removal performance on various stains including greasy stains like sebum, make-up, or lipstick, enzymatic stains like blood, grass or cocoa as well as bleachable stains like wine, coffee or tea, in any laundry application upon ageing of the composition, i.e. when used after prolonged periods of storage after its manufacturing, as compared to the stain removal performance delivered by the same composition without such a stabilising agent, upon ageing of the composition. Also, the use, in a liquid hypohalite bleach-containing composition comprising a surfactant, of such a stabilising agent, provides improved surfactant stability in said composition upon prolonged periods of storage.

- [0007]** A further advantage of the processes of bleaching fabrics according to the present invention is that they are suitable for the bleaching of different types of fabrics including natural fabrics (e.g., fabrics made of cotton, viscose, linen, silk and wool), synthetic fabrics such as those made of polymeric fibers of synthetic origin as well as those made of both natural and synthetic fibers. Indeed, synthetic fibers may be bleached according to the present invention despite a standing prejudice against the use of hypohalite bleaches, especially hypochlorite bleaches, on synthetic fibers, as evidenced by warning on labels of commercially available hypochlorite bleaches and clothes. Advantageously, the compositions used according to the bleaching processes of the present invention are not only safe to the fabrics per se bleached therewith but also to the fabrics colours.

- 45 **[0008]** Advantageously, the liquid bleaching compositions used according to the present invention may be contacted to the fabrics to bleach, in diluted conditions, e.g. when used as a detergent additive or alone as a laundry detergent composition, and/or in neat condition, e.g. when used as a liquid pretreater (spotter).

Background art

- 50 **[0009]** EP-A-668 345 discloses hypochlorite-containing compositions comprising a source of strong alkalinity, a pH buffering means (silicate/carbonate) and radical scavengers. Surfactants are disclosed as optional ingredients without mentioning any, nor levels thereof.

- [0010]** European co-pending application number 97870041.7 discloses bleaching compositions comprising a hypohalite bleach, a pH buffering means and an effective amount of an anionic surfactant. Radical scavengers and chelating agents are mentioned as optional ingredients without specifying any, nor levels thereof.

- [0011]** European co-pending applications numbers 96870088.0 and 96870128.4 disclose hypochlorite-based compositions with surfactants and optionally radical scavengers. Chelants are mentioned as optional ingredients without

specifying any, nor levels thereof. No laundry application is disclosed.

[0012] EP-A-317 066 discloses thickened aqueous cleaning compositions comprising an active cleaning ingredient (hypochlorite, acids, bases (NaOH, carbonate, silicate)), a quaternary ammonium compound, and an organic counterion (e.g. benzoic acid). No laundry application is disclosed.

[0013] US 5384 061 discloses thickened compositions comprising hypochlorite, a cross-linked polycarboxylate polymer, phytic acid, a radical scavenging rheology stabilizing agent, an alkaline buffering agent to provide said composition with a pH above 10. Various surfactants are disclosed. No laundry application is disclosed.

Summary of the invention

[0014] The present invention encompasses a process of bleaching fabrics which comprises the steps of:

- contacting said fabrics with a liquid bleaching composition comprising a hypohalite bleach, from 0.1% to 20% by weight of the total composition of a surfactant and from 0.001% to 10% by weight of a stabilising agent selected from the group consisting of radical scavenger, chelating agent and mixture thereof, in its diluted or neat form,
- allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics,
- and then rinsing said fabrics with water.

[0015] In a preferred embodiment the compositions used in the present invention further comprise a pH buffering component. The presence of a pH buffering component in the compositions herein further contributes to the effective whiteness performance of these compositions as well as to their fabric safety, when used to bleach fabrics. Indeed, the pH buffering component allows to control the alkalinity in the bleaching solution, i.e. maintain the pH of the bleaching solution at a pH of at least 7.5, preferably at least 8.5, and more preferably at least 9.5 for a longer period of time starting from the moment at which the dilution is completed (e.g. when the bleaching composition of the present invention is diluted in the bleaching solution at a dilution level of 200:1 (water:composition)). This buffering action of the pH buffering component reduces the conversion of hypochlorite into hypochlorous acid, one of the species which are most responsible for fabric yellowing and/or fabric damage.

[0016] The present invention further encompasses the use, in a liquid hypohalite bleach-containing composition comprising a surfactant, of a stabilizing agent selected from the group consisting of radical scavenger, chelating agent and mixture thereof, for effective stain removal performance of said composition upon ageing of the composition.

Detailed description of the invention

[0017] The present invention encompasses a process of bleaching fabrics with a bleaching composition as described herein after.

[0018] By "fabrics", it is to be understood any types of fabrics including for example clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like.

[0019] The process of bleaching fabrics herein is suitable for both natural fabrics and synthetic fabrics. By "natural" fabrics, it is meant fabrics made of cotton, viscose, linene, silk and/or wool. By "synthetic" fabrics, it is meant those made of synthetic fibers like polymeric fibers (polyamide, polyester, lycra® and elastane®), and those made of both natural and synthetic fibers.

[0020] The process of bleaching fabrics according to the present invention comprises the steps of contacting said fabrics with a liquid bleaching composition comprising a hypohalite bleach, a surfactant (0.1%-20%) and a stabilizing agent as defined herein after (0.001%-10%). In a preferred embodiment, the compositions used in the process of bleaching fabrics herein are liquid hypochlorite-containing compositions that may further comprise a pH buffering component as defined hereinafter. Said process of bleaching according to the present invention delivers effective stain removal performance upon ageing of the compositions.

[0021] The liquid compositions according to the present invention are contacted to fabrics in their neat or diluted form.

[0022] The compositions according to the present invention are typically used in diluted form in a laundry operation. By "in diluted form", it is meant herein that the compositions for the bleaching of fabrics according to the present invention may be diluted by the user, preferably with water. Such dilution may occur for instance in hand laundry applications as well as by other means such as in a washing machine. Said compositions can be diluted up to 500 times, preferably from 5 to 200 times and more preferably from 10 to 80 times.

[0023] More specifically, the process of bleaching fabrics according to the present invention comprises the steps of first contacting said fabrics with a liquid bleaching composition as described herein, in its diluted form, then allowing said fabrics to remain in contact with said composition, for a period of time sufficient to bleach said fabrics, typically 1 to 60 minutes, preferably 5 to 30 minutes, then rinsing said fabrics in water. If said fabrics are to be washed, i.e., with a

conventional composition comprising at least one surface active agent, said washing may be conducted together with the bleaching of said fabrics by contacting said fabrics at the same time with a bleaching composition according to the present invention and said detergent composition, or said washing may be conducted before or after that said fabrics have been bleached. Accordingly, the process according to the present invention allows to bleach fabrics and optionally to wash fabrics with a detergent composition comprising at least one surface active agent before the step of contacting said fabrics with the liquid bleaching composition as described herein and/or in the step where said fabrics are contacted with the bleaching composition and/or after the step where said fabrics are contacted with the bleaching composition and before the rinsing step, and/or after the rinsing step.

[0024] In another embodiment of the present invention the process of bleaching fabrics comprises the step of contacting fabrics with a liquid bleaching composition as described herein after, in its neat form, of allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics, typically 5 seconds to 30 minutes, preferably 1 minute to 10 minutes and then rinsing said fabrics in water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted before or after that said fabrics have been bleached. In the embodiment of the present invention wherein the liquid bleaching composition used according to the present invention, is contacted to the fabrics in its neat form, it is preferred that the level of hypochlorite bleach, is from 0.01 % to 5%, preferably from 0.1 % to 3.5%, more preferably from 0.2% to 2% and most preferably from 0.2% to 1%. Advantageously, the present invention provides a process of bleaching fabrics wherein liquid hypochlorite bleach-containing compositions are applied neat onto a fabric to bleach, despite a standing prejudice against using hypochlorite-containing compositions neat on fabrics.

[0025] It is preferred to perform the bleaching processes herein before said fabrics are washed. Indeed, it has been observed that bleaching said fabrics with the compositions herein (diluted and/or neat bleaching methods) prior to washing them with a detergent composition provides superior whiteness and stain removal with less energy and detergent than if said fabrics are washed first, then bleached.

[0026] Alternatively, instead of following the neat bleaching process as described herein above (pretreater application) by a rinsing step with water and/or a conventional washing step with a liquid or powder conventional detergent, the bleaching pre-treatment operation may also be followed by the diluted bleaching process as described herein before either in bucket (hand operation) or in a washing machine.

[0027] The temperatures at which the bleaching process herein is performed, do have an influence on the stain removal performance delivered. More specifically, an increased temperature accelerates the bleaching process, i.e. diminishes the time required to bleach a given soil. Typically, the bleaching solutions occurring in the bleaching processes according to the present invention where the bleaching compositions herein are used in their diluted form have a temperature of from 4°C to 60°C, preferably from 10°C to 50°C and most preferably from 20°C to 40°C.

[0028] The compositions for use in these bleaching processes are in liquid form. Preferably, these compositions are in liquid aqueous form. More preferably, they comprise water in an amount of from 60% to 98% by weight, more preferably of from 80% to 97% and most preferably of from 85% to 97% by weight of the total aqueous liquid bleaching composition.

Hypochlorite bleach

[0029] An essential component of the invention is a hypochlorite bleach. Hypochlorite bleaches may be provided by a variety of sources, including bleaches that are oxidative bleaches and subsequently lead to the formation of positive halide ions as well as bleaches that are organic based sources of halides such as chloroisocyanurates.

[0030] Suitable hypochlorite bleaches for use herein include the alkali metal and alkaline earth metal hypochlorites, hypobromites, hypoiodites, chlorinated trisodium phosphate dodecahydrates, potassium and sodium dichloroisocyanurates, potassium and sodium trichlorocyanurates, N-chloroimides, N-chloroamides, N-chloroamines and chlorohydrates.

[0031] For the liquid compositions herein, the preferred hypochlorite bleaches among the above described are the alkali metal and/or alkaline earth metal hypochlorites selected from the group consisting of sodium, potassium, magnesium, lithium and calcium hypochlorites, and mixtures thereof, more preferably the alkali metal sodium hypochlorite.

[0032] Preferably, the liquid compositions used according to the present invention comprise said hypochlorite bleach such that the content of active halide in the composition is of from 0.1% to 20% by weight, more preferably from 0.25% to 8% by weight, most preferably from 0.5% to 6% by weight of the composition.

The surfactant

[0033] An essential component of the invention is a surfactant or mixture thereof. Said surfactant is present in the compositions used according to the present invention in amounts of from 0.1% to 20% by weight of the total composition, preferably of from 0.1% to 15%, more preferably from 1% to 10% and most preferably from 2% to 8%.

[0034] Surfactants for use herein include anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof. Naturally, for the purpose of the invention, the surfactants have to be stable to the hypochlorite bleach.

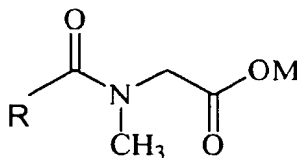
[0035] Surfactants are essential ingredients herein as they deliver the desired stain removal performance on the fabrics bleached.

[0036] Suitable anionic surfactants for use herein include water-soluble salts or acids of the formula ROSO_3M wherein R preferably is a $\text{C}_4\text{-C}_{24}$ hydrocarbyl, preferably linear or branched alkyl having a $\text{C}_6\text{-C}_{20}$ alkyl component, more preferably a $\text{C}_8\text{-C}_{18}$ linear or branched alkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0037] Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula $\text{RO(A)}_m\text{SO}_3\text{M}$ wherein R is a linear or branched alkyl group having a $\text{C}_4\text{-C}_{24}$ alkyl component, preferably a $\text{C}_8\text{-C}_{20}$ linear or branched alkyl, more preferably $\text{C}_{10}\text{-C}_{18}$ linear or branched alkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 30, more preferably between about 0.5 and about 5, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (1.0) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(1.0)$ -sulfate, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate-(2.25) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(2.25)$ -sulfate, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (3.0) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(3.0)$ sulfate, and $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (4.0) sulfate, $\text{C}_{12}\text{-C}_{18}\text{E}(4.0)$ sulfate, wherein the counterion is conveniently selected from sodium and potassium.

[0038] Other anionic surfactants useful for detergent purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, $\text{C}_4\text{-C}_{24}$ linear alkylbenzenesulfonates, $\text{C}_8\text{-C}_{22}$ primary or secondary alkanesulfonates, $\text{C}_8\text{-C}_{24}$ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, $\text{C}_8\text{-C}_{24}$ alkylpolyglycol ethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_{12}\text{-C}_{18}$ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_6\text{-C}_{14}$ diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the non-ionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{COO-M}^+$ wherein R is a $\text{C}_8\text{-C}_{22}$ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975, to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

[0039] Other suitable anionic surfactants for use herein also include acyl sarcosinate or mixtures thereof, in its acid and/or salt form, preferably long chain acyl sarcosinates having the following formula:



wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Said acyl sarcosinate surfactants are derived from natural fatty acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to be used as aqueous solution of their salt or in their acidic form as powder. Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and completely biodegradable and have good skin compatibility.

[0040] Accordingly, suitable long chain acyl sarcosinates for use herein include C_{12} acyl sarcosinate (i.e., an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and C_{14}

acyl sarcosinate (i.e., an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C₁₂ acyl sarcosinate is commercially available, for example, as Hamposyl L-30[®] supplied by Hampshire. C₁₄ acyl sarcosinate is commercially available, for example, as Hamposyl M-30[®] supplied by Hampshire.

[0041] In a preferred embodiment of the present invention the compositions for use in the bleaching process of the present invention comprise at least an anionic surfactant, especially an alkylbenzenesulphonate, alkylsulphate, alkyl alkoxy (preferably ethoxy) sulphate and/or alkylethoxycarboxylate with an alkyl chain containing from 4 to 24 carbon atoms, preferably from 8 to 18, most preferably from 8 to 16. Indeed, such anionic surfactants have been found to provide good stain removal performance as well as to improve the whiteness to fabrics which are treated according to the process herein, with a bleaching composition comprising them.

[0042] The whitening effect, i.e. the yellowing-prevention effect, can be determined by both visual and instrumental grading. Visually, the difference in yellowing between items treated with different compositions can be determined by a team of expert panellists. Instrumentally, the assessment can be determined with the Spectraflash[®] SF 500, Machbet White-eye[®] 500) or a ZEISS ELREPHO[®] or others which are available for instance from Hunterlab[®] or Gardner[®].

[0043] In a particular embodiment of the present invention the surfactant system used is an anionic surfactant system, namely alkyl alkoxy (preferably ethoxy) sulphate like alkyl (ethoxy) 3 sulphate alone or together with a co-surfactant, preferably a C4-C18 alkyl sulphate and/or a C8-C18 alkyl or aryl sulphonate like C8-C18 benzene sulphonate and/or another alkyl alkoxy sulphate apart the 3 ethoxylated one. Indeed, the presence of said alkyl (ethoxy) 3 sulphate alone or together with a cosurfactant provides the desired viscosity to the compositions suitable for use according to the process of bleaching of the present invention, and delivers excellent stain removal properties to said compositions when used in any laundry application herein.

[0044] Typically, such compositions suitable for use herein have a viscosity between 25 cps and 1500 cps, preferably between 50 cps and 1100 cps, depending from the ratio between AE₃S and the co-surfactant, when measured with the following viscosity parameter: angle :1°58, gap : 60, diameter : 4.0 cm and iner :63.60 at a temperature of 25°C and a shear rate of 30 1/sec.

[0045] Also mixture of anionic surfactants and other surfactants especially zwitterionic surfactants like betaine surfactants are also suitable herein.

[0046] Suitable nonionic surfactants for use herein include a class of compounds which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or secondary alcohol) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

[0047] Accordingly suitable nonionic synthetic surfactants include :

(i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 20 carbon atoms in either a straight chain or branched chain configuration, preferably from 8 to 12 carbon atoms, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane;

(ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000;

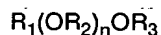
(iii) The condensation product of aliphatic alcohols having from 6 to 22 carbon atoms, in either straight chain or branched chain configuration, preferably from 8 to 18 carbon atoms, with from 2 to 35 moles of ethylene oxide, preferably from 4 to 25 and more preferably from 5 to 18. Example of this type of material are a coconut alcohol ethylene oxide condensate having from 5 to 18 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 9 to 14 carbon atoms;

(iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; specific example is tetradecyl dimethyl phosphine oxide;

(v) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol; The hydrophobic portion of these compounds will preferably have a molecular weight

of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide.

[0048] Particularly suitable nonionic surfactants for use herein are capped nonionic ethoxylated surfactants according to the formula:



wherein R_1 is a C_8 - C_{18} linear or branched alkyl or alkenyl group, aryl group, alkaryl group, preferably, R_1 is a C_{10} - C_{15} alkyl or alkenyl group, more preferably a C_{10} - C_{15} alkyl group;

R_2 is a C_2 - C_{10} linear or branched alkyl group, preferably a C_4 group;

R_3 is a C_1 - C_{10} alkyl or alkenyl group, preferably a C_1 - C_5 alkyl group, and

n is an integer ranging in the range of from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5; or mixtures thereof.

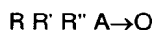
[0049] These surfactants are commercially available from BASF under the trade name Plurafac[®], from HOECHST under the trade name Genapol[®] or from ICI under the trade name Symperonic[®]. Preferred capped nonionic ethoxylated surfactant of the above formula are those commercially available under the tradename Genapol[®] L 2.5 NR from Hoechst, and Symperonic[®] LF/CS 1.100 from ICI.

[0050] Other suitable nonionic surfactants for use herein include the amine oxides corresponding to the formula:



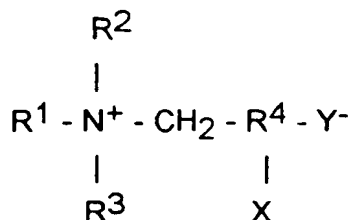
wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. The preferred amine oxides are those in which the primary alkyl group has a straight chain in at least most of the molecules, generally at least 70%, preferably at least 90% of the molecules, and the amine oxides which are especially preferred are those in which R contains 10-18 carbons and R' and R'' are both methyl. Exemplary of the preferred amine oxides are the N-hexyldimethylamine oxide, N-octyldimethylamine oxide, N-decyldimethylamine oxide, N-dodecyl dimethylamine oxide, N-tetradecyldimethylamine oxide, N-hexadecyl dimethylamine oxide, N-octadecyldimethylamine oxide, N-eicosyldimethylamine oxide, N-docosyldimethylamine oxide, N-tetracosyl dimethylamine oxide, the corresponding amine oxides in which one or both of the methyl groups are replaced with ethyl or 2-hydroxyethyl groups and mixtures thereof. A most preferred amine oxide for use herein is N-decyldimethylamine oxide.

[0051] Other suitable nonionic surfactants for the purpose of the invention are the phosphine or sulfoxide surfactants of formula:



wherein A is phosphorus or sulfur atom, R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently selected from methyl, ethyl and 2-hydroxyethyl. The arrow in the formula is a conventional representation of a semi-polar bond.

[0052] Suitable zwitterionic detergents for use herein comprise the betaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these detergents are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference. Preferred zwitterionic detergent compounds have the formula:

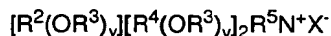


wherein R¹ is an alkyl radical containing from 8 to 22 carbon atoms, R² and R³ contain from 1 to 3 carbon atoms, R⁴ is an alkylene chain containing from 1 to 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R¹, R² and R³ radicals is from 14 to 24 carbon atoms.

[0053] Amphoteric and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system are represented by detergents such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378, said patents being incorporated herein by reference.

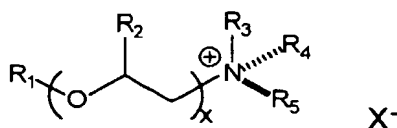
[0054] Additional synthetic detergents and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1980, incorporated herein by reference.

[0055] Cationic surfactants suitable for use in compositions of the present invention are those having a long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:



wherein R² is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, benzyl ring structures formed by joining the two R⁴ groups, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

[0056] Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R¹ is a short chainlength alkyl (C₆-C₁₀)

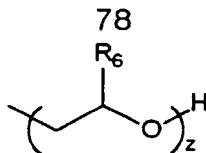
y is 2-4, preferably 3.

whereby R² is H or a C₁-C₃ alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R³, R⁴ and R⁵ are either the same or different and can be either a short chain alkyl (C₁-C₃) or alkoxyated alkyl of the formula II,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula II

R₆ is C₁-C₄ and z is 1 or 2.

[0057] Preferred quat ammonium surfactants are those as defined in formula I whereby

R₁ is C₈, C₁₀ or mixtures thereof, x=0,
R₃, R₄, R₅ = CH₃.

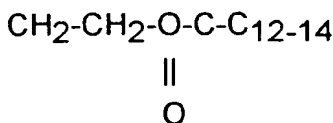
[0058] Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds having the formula :



wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, benzyl, and -(C₂H₄)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

[0059] The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂, R₃ and R₄ are methyl and the anion X may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
C₁₂₋₁₅ trimethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R₁ is



alkyl and R₂, R₃, R₄ are methyl).
di-alkyl imidazolines.

[0060] Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

The stabilising agent

[0061] An essential component of the invention is a stabilising agent being a radical scavenger, a chelating agent or a mixture thereof. Naturally, for the purpose of the invention, the stabilizing agents have to be stable to the hypohalite bleach.

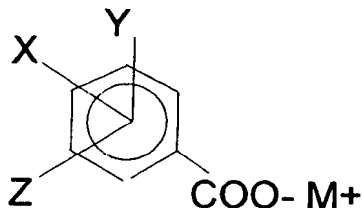
[0062] Highly preferred in the liquid bleaching compositions for use according to the present invention as the stabilising agent is a radical scavenger or a mixture thereof alone, or together with a chelating agent or a mixture thereof.

[0063] Suitable radical scavengers for use herein include aromatic radical scavengers comprising an unsaturated ring

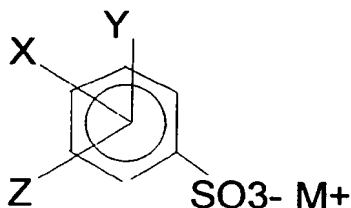
system of from 3 to 20 carbon atoms, preferably of from 3 to 18 and more preferably of from 5 to 14 and having a double bond set comprising a total of $4n+2$ electrons, wherein n is an integer of from 0 to 4, preferably of from 1 to 3. Indeed said aromatic radical scavengers include benzene derivatives, naphthalene derivatives, annulene derivatives, cyclopentadiene derivatives, cyclopropene derivatives and the like, especially aryl carboxylates and/or aryl sulfonates.

[0064] Particularly suitable radical scavengers (aryl carboxylates, aryl sulphonate and derivatives thereof) for use in the present invention have one of the following formulas:

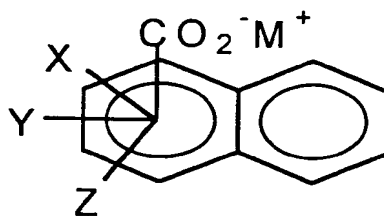
(a)



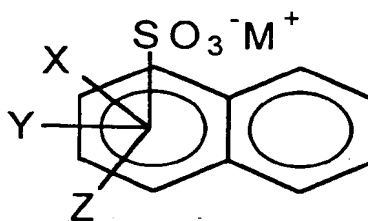
(b)



(c)



(d)



wherein each X, Y, and Z are -H, -COO-M⁺, -Cl, -Br, -SO₃-M⁺, -NO₂, -OCH₃, or a C₁ to C₁₀ primary and secondary alkyl groups and M is H or an alkali metal, or mixtures thereof. Examples of these components include pyromellitic acid, i.e. where X, Y and Z are -COO-H⁺; hemimellitic acid, trimellitic acid, i.e. where X and Y are -COO-H⁺ and Z is H. Preferred to be used in the present invention as radical scavengers are phthalic acid; sulfophthalic acid; other mono-substituted phthalic acids; di-substituted benzoic acids; alkyl-, chloro-, bromo-, sulfo-, nitro- or alkoxy- benzoic acids, i.e. where Y

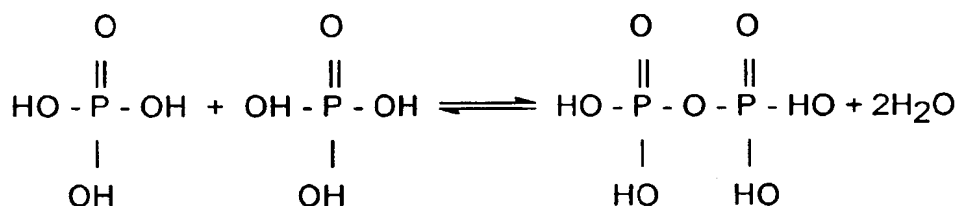
and Z are -H and X is a C₁ to C₁₀ primary and secondary alkyl groups, -Cl, -Br, -SO₃-H⁺, -NO₂ or -OCH₃ (anisic acid) respectively and substituted sulfonic acids. Highly preferred examples of the radical scavengers useful in the present invention are benzoic acid, methoxy benzoic acid, toluic acid, 4-toluene sulfonic acid, 3-nitro benzoic acid, 2 n-octyl benzoic acid, 2 n-octyl sulfonic acid, anisic acid or mixtures thereof. Most preferred herein are benzoic acid and/or methoxy benzoic acid and/or 3-nitrobenzoic acid.

[0065] All the radical scavengers described above are the acidic form of the species, i.e. M is H. It is intended that the present invention also covers the salt derivatives of these species, i.e. M is an alkali metal, preferably sodium or potassium. In fact, since the pH of the compositions of the present invention is in the alkaline range, the radical scavengers of the present invention exist primarily as the ionized salt in the aqueous composition herein. The anhydrous derivatives of certain species described herein above can also be used in the present invention, e.g. pyromellitic dianhydride, phthalic anhydride, sulphthalic anhydride and the like.

[0066] Suitable chelating agents for use herein may be any of those known to those skilled in the art such as the ones selected from the group comprising phosphonate chelating agents, phosphate chelating agents, polyfunctionally-substituted aromatic chelating agents, ethylenediamine N,N'-disuccinic acids, or mixtures thereof.

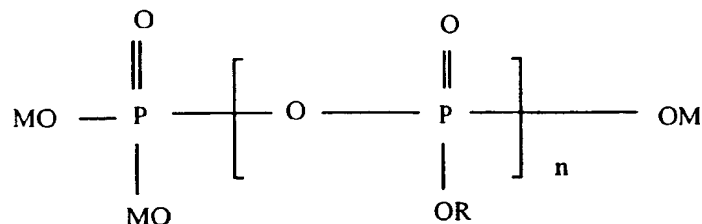
[0067] Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents for use herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

[0068] Suitable phosphate chelating agents are as following: Phosphonic acid can be condensed in the reaction

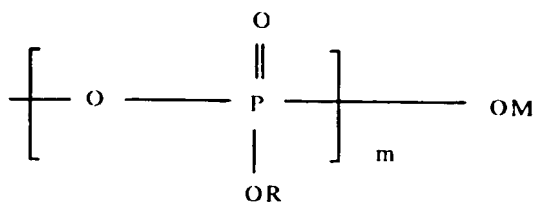


[0069] The reaction can be repeated with any of the reactive OH groups, and phosphate ingredients are obtained which can be

- linear or branched polyphosphates of structure



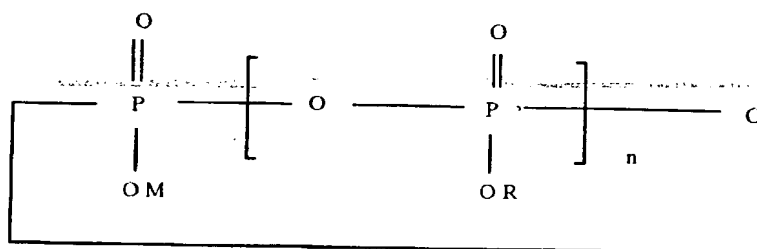
- when R is M or



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- when M is a counterion, preferably alkali metal;
- when $0 \leq n+m < 500$ (if $n+m = 0$ then the compound is phosphonic acid)
- cyclic polyphosphates (also referred to as metaphosphates), of structure

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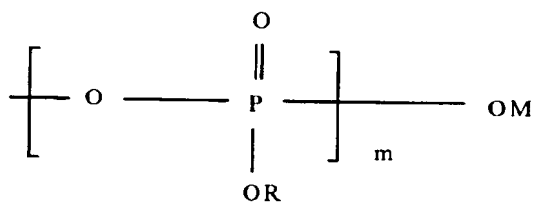


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- when R is M or

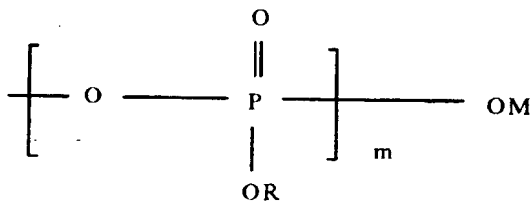
35



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- if R is

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the phosphate compound contains both cycles and branched chain, and can be referred to as an ultraphosphate.)

- where M is a counterion, preferably an alkali metal

- where $0 \leq n+m < 500$

[0070] All such phosphate ingredients are suitable for use herein, and preferred are linear phosphate ingredients (i.e. R is M) where n is 1 (pyrophosphate) and n is 2 (tripolyphosphate (STPP)), most preferably where n is 2. The most commonly available form of these phosphate is where M is Sodium.

[0071] Phytic acid, which is a chelating agent particularly suitable for use herein, is a hexa-phosphoric acid that occurs naturally in the seeds of many cereal grains, generally in the form of the insoluble calcium-magnesium salt. It may also be derived from corn steep liquor. Commercial grade phytic acid is commercially available from J.T.Baker Co., e.g. as a 40% aqueous solution. It is intended that the present invention covers the acidic form of phytic acid as well as alkali metal salt derivatives thereof, particularly sodium or potassium salts thereof. Sodium phytate is available from Jonas Chemical Co (Brooklyn, N.Y.). In fact since the typical pH of the compositions of the present invention are in the alkaline pH range, the phytic acid component exists primarily as the ionized salt in the liquid compositions herein even if it is added in its acidic form. Mixtures of such salts of phytic acid are also covered.

[0072] Polyfunctionally-substituted aromatic chelating agents may also be useful herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

[0073] A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'-disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4,704,233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

[0074] Particularly preferred chelating agents for use herein are phosphate chelating agents like sodium tripolyphosphate, sodium pyrophosphate, phytic acid, and mixtures thereof. Indeed, these chelating agents when present in the bleaching compositions used to bleach fabrics herein have been found to further participate to the excellent stain removal performance delivered by these compositions upon ageing of the compositions.

[0075] Typically, the compositions for use herein comprise from 0.01% to 10% by weight of the total composition of a stabilising agent, or mixtures thereof, preferably from 0.01% to 8% by weight, more preferably from 0.1% to 5%, and most preferably from 0.2% to 3%.

[0076] The present invention is based on the finding that the addition of a stabilizing agent, preferably a radical scavenger alone or together with a chelating agent, in a liquid bleaching composition comprising a hypohalite bleach and a surfactant results in effective stain removal performance of the aged composition when used in any laundry application.

[0077] By "effective" stain removal performance, it is to be understood that the stain removal performance delivered on fabrics bleached with an aged composition according to the present invention is improved, as compared to the stain removal performance delivered by the same composition, but without such a stabilizing agent as mentioned herein before in the same aged condition. In other words, the present invention allows to maintain excellent stain removal performance after prolonged periods of storage time, as compared to the same composition but without said stabilizing agent.

[0078] The stain removal performance upon ageing of the composition in the process of bleaching according to the present invention can be measured by comparison to the same bleaching process wherein the composition used is free of said stabilizing agent (e.g. after 3 months of storage at ambient temperature (around 25°C) after the manufacturing of these compositions).

[0079] The stain removal performance can be determined by visual grading on a scale of for example four grades. This test can be conducted on commercially available stained items (e.g. from WFK Germany or EMPA Switzerland) or on realistic soiled items.

pH

[0080] The pH of the liquid compositions used according to the present invention, as is, is typically from 12 to 14 measured at 25°C. The liquid compositions for use according to the processes of bleaching of the invention have a pH of from 7.5 to 13, preferably from 8 to 12, more preferably from 8.5 to 11.5, when diluted into 1 to 500 times its weight of water. It is in this alkaline range that the optimum stability and performance of the hypohalite as well as fabric whiteness and/or safety are obtained. The pH range is suitably provided by the hypohalite bleach mentioned hereinbefore and optionally the pH buffering component when present, which are alkalis. However, in addition to these components, a strong source of alkalinity may also optionally be used.

[0081] Suitable sources of alkalinity are the caustic alkalis such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such as sodium and/or potassium oxide. A preferred strong source of alkalinity is a caustic alkali, more preferably sodium hydroxide and/or potassium hydroxide. Typical levels of such caustic alkalis, when present, are of from 0.1% to 1.5% by weight, preferably from 0.5% to 1.5% by weight of the composi-

tion.

Optional pH buffering components

5 [0082] In the compositions used according to the present invention, the presence of a pH buffering component is not compulsory, but is highly preferred.

[0083] The pH buffering component ensures that the pH of the composition is buffered to a pH value ranging from 7.5 to 13, preferably from 8 to 12, more preferably from 8.5 to 11.5 after the composition has been diluted into 1 to 500 times its weight of water.

10 [0084] Suitable pH buffering components for use herein are selected from the group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, boron salts, phosphates, stannates, alluminates and mixtures thereof. The preferred alkali metal salts for use herein are sodium and potassium.

[0085] Suitable boron salts or mixtures thereof for use herein include alkali metal salts of borates and alkyl borates and mixtures thereof. Examples of boron salts include boric acid, alkali metal salts of metaborate, tetraborate, octoborate, pentaborate, dodecaboron, borontrifluoride and alkyl borate containing from 1 to 12 carbon atoms, preferably from 1 to 4. Suitable alkyl borate includes methyl borate, ethyl borate and propyl borate. Particularly preferred boron salts herein are the alkali metal salts of metaborate, such as sodium metaborate, potassium metaborate, and the alkali metal salts of borate, such as sodium borate, or mixtures thereof. Boron salts like sodium metaborate and sodium tetraborate are commercially available from Borax and Societa Chimica Larderello under the name sodium metaborate and Borax®.

[0086] Particularly preferred pH buffering components are selected from the group consisting of sodium carbonate, sodium silicate, sodium borate, sodium metaborate and mixtures thereof.

[0087] The raw materials involved in the preparation of hypochlorite bleaches usually contain by-products, e.g calcium carbonate resulting in an amount of up to 0.4% by weight of by-product within the hypochlorite composition. However, at such amount, the by-product will not have the buffering action defined above.

25 [0088] Liquid bleaching compositions for use herein will typically contain an amount of pH buffering component of from 0.5% to 9% by weight, preferably from 0.5% to 5% by weight, and more preferably in an amount of from 0.6% to 3% by weight of the composition.

[0089] The compositions according to the invention may comprise other optional components such as organic or inorganic alkalis, builders, thickening agents, polymers, pigments, dyes, solvents, perfumes, brighteners and mixtures thereof.

Optional brighteners

35 [0090] Any brighteners known to those skilled in the art may be used herein including both hydrophobic and hydrophilic brighteners and mixtures thereof. Naturally, for the purpose of the invention, the brightener has to be stable to the hypochlorite bleach. The brighteners may be desired herein to further enhance the whiteness performance of the compositions herein.

[0091] Brighteners are compounds which have the ability to fluorescent by absorbing ultraviolet wave-lengths of light and re-emitting visible light. Brighteners, also referred to as fluorescent whitening agent (FWA), have been extensively described in the art, see for instance EP-A-0 265 041, EP-A-0 322 564, EP-A-0 317 979 or "Fluorescent whitening agents" by A.K. Sarkar, published by MERROW, especially page 71-72.

[0092] Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methine-cyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Further optical brighteners which may also be used in the present invention include naphthlimide, benzoxazole, benzofuran, benzimidazole and any mixtures thereof.

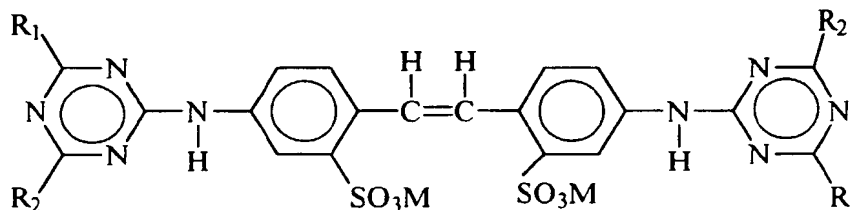
50 [0093] Examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856. These brighteners include the PHORWHITE® series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal-UNPA®, Tinopal CBS® and Tinopal 5BM® available from Ciba-Geigy; Artic White CC® and Artic White CWD®; the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bispheyls; and the aminocoumarins.

55 [0094] Specific examples of brighteners useful herein include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho-[1,2-d]oxazole; 2-(stilbene-4-yl)-2H-naphtho[1,2-d]triazole, 3-phenyl-7-(isoindolyl) coumarin; 3-methyl-7-(isoindolyl) coumarin; 3-chloro-7-(isoindolyl) coumarin; 4-(isoindolyl)-4'-methylstilbene; 4-(isoindolyl)-4'-methoxystilbene; sodium 4-(isoindolyl)-4'-methoxystilbene; and sodium 4-(isoindolyl)-4'-methoxystilbene.

doliny)-4'-stilbenesulfonate; 4-(isoindoliny)-4'-phenylstilbene; 4-(isoindoliny)-3-methoxy-4'-methylstilbene; 4-(2-chloroisoindoliny)-4'-(2-methylisoindoliny)-2,2'-stilbenedisulfonic acid; disodium 4,4'-diisoindoliny-2,2'-stilbene disulfonate; 4,4'-diisoindoliny-2,2'-stilbenedisulfonamide; disodium 4,4'-(7,8-dichloro-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(7-chloro-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(6-isopropoxy-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(7,8-diisopropyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(7-butoxy-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(6-trifluoromethyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-[6-(1,4,7-trioxanonyl)-1-isoindoliny]2,2'-stilbenedisulfonate; disodium 4,4'-(7-methoxymethyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(6-phenyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(6-naphthyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(6-methylsulfonyl-1-isoindoliny)2,2'-stilbenedisulfonate; disodium 4,4'-(7-cyano-1-isoindoliny)2,2'-stilbenedisulfonate; and disodium 4,4'-[7-(1,2,3-trihydroxypropyl)-1-isoindoliny]2,2'-stilbenedisulfonate; disodium 4-isoindoliny-4'-ethoxy-2,2'-stilbenedisulfonate; disodium 4-isoindoliny-4'-methoxy-2,2'-stilbenedisulfonate; disodium 4-isoindoliny-4'-ethoxy-2,2'-stilbenedisulfonamide; disodium 4-isoindoliny-4'-methyl-2,2'-stilbenedisulfonamide; 4,4'-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2'-stilbenedisulfonic acid and mixture thereof. See also U.S. Patent 3,646,015, U.S. Patent 3,346,502 and U.S. Patent 3,393,153 for further examples of brighteners useful herein.

[0095] Indeed one of the functionally equivalent derivative salts of 4,4'-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2'-stilbenedisulfonic acid, namely its sodium salt is available from Mobay Chemical Corporation, a subsidiary of Bayer AG under the name Phorwite® CAN. The amine salt is available from Molay under the name Phorwite® CL solution. The potassium salt is available under the name Phorwite® BHC 766.

[0096] Specific examples of hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

[0097] When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

[0098] When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

[0099] When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

[0100] Other substituted stilbene 2,2'-disulfonic acid derivatives also include 4-4'-bis (2-2' styryl sulfonate) biphenyl, commercially available from Ciba-Geigy under the trade name Brightener 49® or other hydrophilic brighteners like for example Brightener 3® or Brightener 47®, also commercially available from Ciba-Geigy.

[0101] Specific examples of hydrophobic brighteners useful in the present invention include the polycyclic oxazole derivatives such as benzo-oxazole derivatives, or mixtures thereof and particularly preferred herein the benzo-oxazole derivatives. An example of such a brightener is benzoxazole,2,2'-(thiophenaldyl)bis having the following formula C₁₈H₁₀N₂O₂S, commercially available from Ciba-Geigy under the trade name Tinopal SOP®. This brightener is almost insoluble in water, i.e. it has a solubility being lower than 1 gram per liter. Another example of such a brightener is bis(sulfobenzofuranyl)biphenyl, commercially available from Ciba-Geigy under the trade name Tinopal PLC®.

[0102] By "hydrophobic brighteners", it is to be understood herein any brightener whose solubility in water is lower than 10 grams per liter at 25°C. By "solubility" of a given compound, it is to be understood herein the amount of said

compound solubilized in deionized water at 25°C. Thus, a compound having a solubility being lower than 10 grams per liter means that when less than 10 grams of said given compound is incorporated in deionized water at 25°C said compound is entirely dissolved in said water, i.e. a clear and stable solution is obtained. In other words, incorporating 10 grams per liter or more of said given compound in water will result in a precipitation of said compound in said medium.

Accordingly, by "hydrophilic brighteners", it is to be understood herein any brightener whose solubility in water is higher or equal to 10 grams per liter at 25°C.

[0103] Typically the compositions used according to the present invention comprise up to 1.0% by weight of the total composition of a brightener or a mixture thereof, preferably from 0.005% to 0.5%, more preferably from 0.005% to 0.3% and most preferably from 0.008% to 0.1%.

[0104] Where hydrophobic brighteners are present in the compositions used according to the present invention they may both be solubilized or suspended in the hypohalite bleach-containing compositions of the present invention. Such brighteners solubilisation can be for example achieved by means of a surfactant or a mixture thereof as described herein after. Various surfactants may be used for this purpose like C8-C20 alkyl aryl sulphonates as described for example in U.S. Patent 4, 623,476 or amine oxides as described for example in EPA-186386. Preferred surfactants also called "co-surfactants" to solubilise and/or suspend such a hydrophobic brightener are anionic surfactants including alkyl sulphates or alkylalkoxy sulphates having from 4 to 30 carbon atoms in the alkyl chain, or alkylethoxycarboxylates having from 6 to 30 carbon atoms in the alkyl chain such as AkypoSoft® 100 NV from Chemy or Sandosan LNCS from Sandoz. Preferred are C12-C14 alkylethoxysulphates. Such co-surfactants herein should be used in amounts required to solubilize the hydrophobic brightener in need thereof.

[0105] Generally, when a co-surfactant is used, the liquid compositions for use herein are prepared in a process wherein the hydrophobic brightener and the co-surfactant are first mixed to form a premix, before the premix is then mixed with the remainder of the composition which has been separately prepared.

[0106] Alternatively the hydrophobic brightener may be suspended by means of a specific suspending agent, like polymers and/or colloidal particulate silicate. Any polymers known to those skilled in the art as having suspending properties are suitable for use herein including those described for example in EP-A-206718.

Optional polymers

[0107] An optional component of the compositions for herein is a polymer. That polymer, has surprisingly been found to also reduce the yellowing of the fabrics treated therewith, i.e. improve whiteness, as well as improve fabric safety. Naturally, for the purpose of the invention, the polymer has to be stable to the hypohalite bleach.

[0108] Suitable polymers for use are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids, polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Co-polymerisation of the above monomeric units among them or with other co-monomers such as styrenesulfonic acid is also suitable.

[0109] Preferred examples of such polymers are the polymers and co-polymers of monomeric units selected from the group consisting of acrylic acid, maleic acid, vinylsulphonic acid and mixtures thereof. Also suitable for use herein are the above mentioned polymers and co-polymers which are modified in order to contain other functional groups such as aminophosphonic and/or phosphonic units. More preferred polymers are selected from the group consisting of polyacrylate polymers, co-polymers of acrylic and maleic acid, co-polymers of styrene sulphonic acid and maleic acid, and mixtures thereof, preferably modified with aminophosphonic and/or phosphonic groups.

[0110] The molecular weight for these polymers and co-polymers is preferably below 100,000, most preferably between 500 and 50,000. Most suitable polymers and co-polymers for use herein will be soluble in an amount up to 0.1% by weight, in an aqueous composition comprising 5% by weight of sodium hypochlorite with its pH adjusted to 13 with sodium hydroxide.

[0111] Commercially available such polymers, suitable for use herein, are the polyacrylate polymers sold under the tradename Good-Rite® from BF Goodrich, Acrysol® from Rohm & Haas, Sokalan® from BASF, Norasol® from Norso Haas. Also suitable for use herein are the co-polymers of styrene sulphonic acid and maleic acid, commercially available under the tradename Versaflex® from National Starch such as Versaflex 157, as well as Acumer® terpolymers from Rohm and Haas, in particular Acumer® 3100. Preferred commercially available polymers are the polyacrylate polymers, especially the Norasol® polyacrylate polymers and more preferred are the polyacrylate polymer Norasol® 410N (MW 10,000) and the polyacrylate polymer modified with phosphonic groups Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000).

[0112] A preferred polymer for use herein is a polyacrylate polymer modified with phosphonic groups commercially available under the tradename Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000) from Norso-Haas.

[0113] Mixtures of polymers as herein described may also be used in the present invention.

[0114] Polymers herein are preferably present in low amounts, i.e. in amounts of up to 10%, preferably up to 1% by

weight, more preferably from 0.001% to 0.5% by weight, most preferably from 0.005% to 0.2% by weight of the liquid composition.

Examples

[0115] The invention is illustrated in the following non-limiting examples, in which all percentages are on a weight basis unless otherwise stated.

Composition (weight %)	I	II	III	IV
Sodium hypochlorite	3.5	3.5	3.5	5.0
Sodium hydroxide*	1.25	1.25	1.25	1.00
Sodium carbonate	3.0	3.0	3.0	1.2
Sodium silicate	0.5	0.5	0.5	0.5
Benzoic acid	-	-	1.0	-
Na C12-C14 E3S	7.0	7.0	7.0	7.0
Methoxy benzoate	-	1.0	-	-
Tinopal PLC®	0.01	0.01	0.01	0.01
Sodium tripolyphosphate (STPP)	0.1	0.1	0.1	0.1
Water and minors	up to 100%			

Composition (weight %)	V	VI	VII	VIII
Sodium hypochlorite	5.0	5.0	3.5	3.5
Sodium hydroxide*	1.0	1.0	1.25	1.25
Sodium carbonate	1.25	1.25	3.0	3.0
Sodium silicate	0.5	0.5	0.5	0.5
Benzoic acid	-	1.0	-	-
Na C12-C14 E3S	7.0	7.0	7.0	7.0
Methoxy benzoate	1.0	-	1.0	1.0
Tinopal PLC®	0.01	0.01	0.01	0.01
Phytic acid	-	-	-	1.0
Norasol 440N®	-	-	0.1	0.1
Sodium tripolyphosphate (STPP)	0.1	0.1	-	-
Water and minors	up to 100%			

Composition (weight %)	IX	X	XI	XII
Sodium hypochlorite	3.5	3.5	3.5	3.5
Sodium hydroxide*	1.25	1.25	1.25	1.25
Sodium carbonate	3.0	3.0	3.0	3.0
Sodium silicate	0.5	0.5	0.5	0.5
Benzoic acid	3.0	-	-	-
Sodium borate	-	-	-	3.0
Na C8 sulphate	-	1.0	-	-
Betaine**	-	-	2.0	2.0
Na C12-C14 E3S	7.0	7.0	5.0	5.0
Methoxy benzoate	-	1.0	1.0	1.0
Sodium tripolyphosphate (STPP)	-	0.1	0.1	0.1
Water and minors	up to 100%			

Composition (weight %)	XIII	XIV	XV
Sodium hypochlorite	3.5	3.5	3.5
Sodium hydroxide*	1.25	1.25	1.25
Sodium carbonate	3.0	3.0	3.0
Sodium silicate	0.5	0.5	0.5
Benzoic acid	3.0	-	-
Sodium borate	-	-	-
Na C8 sulphate	-	7.0	-
Nonionic surfactant***	2.5	-	-
Betaine**	2.5	-	5.0
Na C12-C14 E3S	2.5	-	-
Methoxy benzoate	-	1.0	1.0
Sodium tripolyphosphate (STPP)	-	0.1	0.1
Water and minors	up to 100%		

* added NaOH

Tinopal PLC® is bis(sulfobenzenfuranyl)biphenyl available from Ciba Geigy.

Na C12-C14 E3S is an alkyl C12-C14 (ethoxy) 3 sulphate commercially available from Rhone Poulenc and Albright & Wilson.

Benzoic acid is commercially available from Elf Atochem, Enichem, or Albright & Wilson.

Methoxy benzoate is available from Aldrich.

Norasol 440N® is a polyacrylate polymer modified with phosphonic groups (MW 4000) from Norso Haas.

Betaine ** is lauryl dimethyl aminebetaine available from Albright & Wilson.

Nonionic surfactant*** is Plurafac® available from BASF.

[0116] These compositions deliver excellent stain removal performance on various stain including greasy stains, enzymatic stains and/or bleachable stains when used in a laundry application in their neat or diluted form, e.g. 200 times their weight of water, after prolonged periods of storage time, e.g., after 3 months of storage at ambient temperature (25°C) after having been prepared.

Claims

1. A process of bleaching fabrics which comprises the steps of :

- contacting said fabrics with a liquid bleaching composition comprising a hypohalite bleach, from 0.1% to 20% by weight of the total composition of a surfactant and from 0.001% to 10% by weight of a stabilising system being selected from the group consisting of radical scavenger, chelating agent and mixture thereof, in its diluted or neat form,
- allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics,
- then rinsing said fabrics with water.

2. A process of bleaching according to claim 1 wherein the composition is diluted with water at a dilution level up to 500 times its weight, preferably from 5 to 200 times and more preferably from 10 to 80 times

3. A process according to any of the claims 1 or 2 wherein said fabrics are washed with a detergent composition comprising at least one surface active agent before the step of contacting said fabrics with the bleaching composition and/or in the step where said fabrics are contacted with the bleaching composition in diluted form, and/or after the step where said fabrics are contacted with the bleaching composition and before the rinsing step, and/or after the rinsing step.

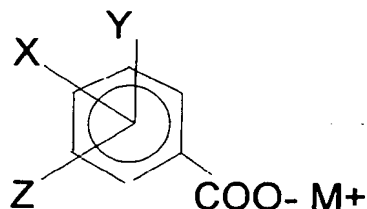
4. A process according to any of the preceding claims, wherein in said bleaching composition said hypohalite bleach is an alkali metal sodium hypochlorite.

5. A process according to any one of the preceding claims, wherein in said bleaching composition said hypohalite, based on active halide, is present in an amount of from 0.1% to 20% by weight, preferably from 0.25% to 8% by weight of the total liquid composition.

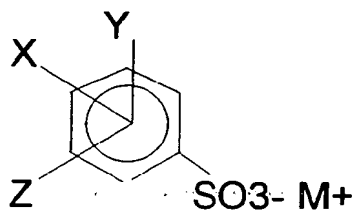
6. A process according to any of the preceding claims wherein in said bleaching composition said stabilising agent is an aromatic radical scavenger or a mixture thereof, preferably a benzene derivative, naphthalene derivative, annu-

lene derivativs, cyclopentadiene derivative, cyclopropene derivative, aryl carboxylate, aryl sulfonate or a mixture thereof, more preferably a radical scavenger having one of the following formulae:

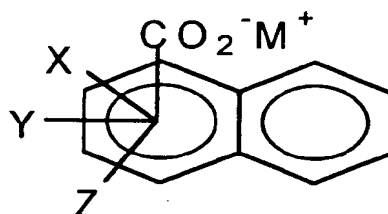
a)



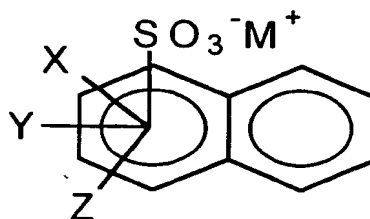
(b)



c)



d)



wherein each X, Y, and Z are -H, -COO-M⁺, -Cl, -Br, -SO₃-M⁺, -NO₂, -OCH₃, or a C₁ to C₁₀ primary and secondary alkyl groups and M is H or an alkali metal, or mixtures thereof, more preferably said radical scavenger is phthalic acid; sulfophthalic acid; another mono-substituted phthalic acid; di-substituted benzoic acid; an alkyl-, chloro-, bromo-, sulfo-, nitro- or alkoxy- benzoic acid, i.e. where Y and Z are -H and X is a C₁ to C₁₀ primary and secondary alkyl groups, -Cl, -Br, -SO₃-H⁺, -NO₂, or -OCH₃ respectively or a substituted sulfonic acid, even more preferably is benzoic acid, methoxy benzoic acid, toluic acid, 4-toluene sulfonic acid, 2 n-octyl benzoic acid, 3-nitro benzoic acid, 2 n-octyl sulfonic acid, anisic acid or mixtures thereof and most preferably is benzoic acid and/or methoxy benzoic acid and/or 3-nitro benzoic acid.

7. A process according to any of the preceding claims, wherein in said bleaching composition said stabilising agent is a chelating agent preferably a phosphonate cheating agent, phosphate cheating agent, polyfunctionally-substituted

aromatic chelating agent, ethylenediamine N,N'-disuccinic acids, or mixtures thereof, more preferably sodium pyrophosphate, sodium tripolyphosphate, and/or phytic acid.

- 5 8. A process according to any one of the preceding claims, wherein in said composition the stabilising agent or mixture thereof, is present in an amount of 0.01% to 8% by weight, more preferably from 0.1% to 5%, and most preferably from 0.2% to 3% by weight of the total liquid composition.
- 10 9. A process according to any one of the preceding claims, wherein in said composition the surfactant is an anionic surfactant, a nonionic surfactant, a zwitterionic surfactant, amphoteric surfactant and/or cationic surfactant, preferably at least an anionic surfactant, more preferably at least an alkylbenzenesulphonate, alkylsulphate, alkylalkoxysulphate or alkylethoxycarboxylate with an alkyl chain containing from 4 to 24 carbon atoms, preferably 8 to 18, most preferably 8 to 16 or mixtures thereof alone or together with another surfactant type.
- 15 10. A process according to any one of the preceding claims, wherein in said composition the surfactant or mixture thereof, is present in an amount of from 0.1 % to 15%, more preferably from 1% to 10% and most preferably from 2% to 8% by weight of the total liquid composition.
- 20 11. A process according to any of the preceding claims wherein said composition further comprises a pH buffering component typically in an amount of 0.5% to 9% by weight of the total composition, preferably from 0.5% to 5% by weight.
- 25 12. A process according to claim 11, wherein said pH buffering component is selected from the group consisting of alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, boron salts, phosphates, stannates, alluminates, and mixtures thereof.
- 30 13. A process according to any of the preceding claims, wherein said composition further comprises a strong source of alkalinity.
- 35 14. A process according to any of the preceding claims, wherein said composition further comprises an optional ingredient selected from the group consisting of builders, thickening agents, polymers, pigments, dyes, solvents, perfumes, brighteners and mixtures thereof.
- 40 15. The use, in a liquid bleaching composition comprising a hypohalite bleach and a surfactant, of stabilizing agent selected from the group consisting of a radical scavenger, a chelating agent, and mixture thereof, for effective stain removal performance upon ageing of the composition.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0140

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 688 857 A (PROCTER & GAMBLE) * page 2, line 56 - page 3, line 4 * * page 3, line 29 - line 47 * * page 4, line 4 - line 36 *	1-15	C11D3/395
D,A	EP 0 668 345 A (PROCTER & GAMBLE) * page 5, line 56 - page 6, line 10 * * page 5, line 6 - line 27 * * claims 1-13 *	1-6,8,9, 11-15	
A	WO 88 05461 A (MOLONY DONALD P) * claims 1-8 *	1-5,9,10	
A	US 5 034 150 A (SMITH WILLIAM L) * claims 1-9 * * column 6, line 41 - column 7, line 9 *	1-5,7,9, 11-15	
A	EP 0 653 482 A (PROCTER & GAMBLE) * claims 1-11 * * page 4, line 4 - line 53 *	1-5,7-9, 11-15	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 January 1998	Examiner Richards, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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